

Chemistry of vinylidene complexes. XXIV. A new μ -vinylidene complex containing RePt core, and platinum-bound carbonyl ligand. Spectroscopic, structural and electrochemical study

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Abstract

The novel heterobinuclear μ -vinylidene complex $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**1**) was isolated from the reaction mixture of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Fe}(\text{CO})_4]$ and $\text{Pt}(\text{PPh}_3)_4$ for the first time. Alternative high-yield synthetic approaches to **1** were developed including the reactions of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)_2]$ (**2**) with $\text{Co}_2(\text{CO})_8$ and $\text{Rh}(\text{acac})(\text{CO})_2$. The complex was characterized by IR and ^1H , ^{13}C and ^{31}P NMR spectroscopy, a molecular structure of **1** was determined by X-ray diffraction analysis. The electrochemical behavior of the new complex was studied by cyclic voltammetry at platinum or glassy carbon electrodes and by dc polarography at a dropping mercury electrode.

Keywords: Rhenium, platinum, vinylidene complexes, heterometallic complexes, electrochemistry

1. Introduction

Organometallic compounds, in which two or more metals linked by hydrocarbon bridge, have attracted considerable attention due to their potential for application in synthesis, catalysis, and material science [1–7]. Understanding interactions between metals and their ligand environment in the heteronuclear organometallic complexes and clusters play an important role in the research of the processes that occur in homogeneous catalytic reactions and on metal surfaces [2,3,7]. The heterometallic vinylidene bridged complexes and clusters are one type of such compounds. They can be easily prepared by reaction of mononuclear vinylidene complexes of the type $\text{L}_n\text{M}=\text{C}=\text{CR}_2$ with unsaturated metal-containing fragments [8,9]. A wide variety of heterometallic vinylidene complexes [9–14] and clusters [8,9] containing MM' , MM'_2 and $\text{MM}'\text{M}''$ cores were obtained by this method.

At the same time, in spite of the tens of known binuclear vinylidene complexes of the type MM' , the compounds containing the terminal CO ligand coordinated to the Pt atom are rare. Moreover, the X-ray structure of only $[\text{cis,cis-Pt}(\text{C}_6\text{F}_5)_2(\text{CO})(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)_2]$ was determined [15]. This homometallic PtPt μ -phenylvinylidene complex and its dimeric analog of the type $[\{\text{cis,cis-(CO)(C}_6\text{F}_5)_2\text{PtPt(PPh}_3)_2\}_2\{\mu_4\text{-1KC}^{\alpha}:2\text{KC}^{\alpha}:3\text{KC}^{\alpha'}:4\text{KC}^{\alpha'}\text{-(1,4-C=CH)}_2\text{C}_6\text{H}_4\}]$ were synthesized by reactions of $[\text{cis-PtR}_2(\text{CO})(\text{thf})]$ with corresponding acetylide and diyne complexes [15,16]. Reactions of bimetallic acyl complex $[(\text{CO})_3\text{Fe}\{\mu\text{-Si(OMe)}_2(\text{OMe})\}(\mu\text{-dppm})\text{Pt}\{\text{C(OMe)}\}]$ with acetylenes led to the series of vinylidene-bridged complexes $[(\text{CO})_3\text{Fe}(\mu\text{-C=CHR})(\mu\text{-dppm})\text{Pt}(\text{CO})]$ ($\text{R} = \text{Ph}, t\text{-Bu}, n\text{-Bu}$) [17]. A related heterobimetallic complex $[(\text{CO})_4\text{W}(\mu\text{-dppm})(\mu\text{-C=CH}_2)\text{Pt}(\text{CO})]$ was prepared by deprotonation of the alkylidene bridged complex $[(\text{CO})_4\text{W}(\mu\text{-dppm})(\mu\text{-CMe})\text{Pt}(\text{CO})][\text{BF}_4]$ with $\text{K}[\text{BH}(\text{CHMeEt})_3]$ [18].

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Another route to the heterobimetallic complexes with the platinum-bound CO ligands is ligand exchange reactions [19,20]. Such ligand exchange can be performed in two main ways: by a treatment of the initial complex with gaseous carbon monoxide [20,21], or by a reaction of one with metal carbonyl compounds [19,22,23]. It should be noted that the carbon monoxide can initiate a cleavage of metal-metal bond and lead to decomposition of starting compound, for example, reactions of μ -carbene complexes with CO lead to formation of triangular clusters containing Pt_3 cores [24–26]. Reactions with metal carbonyl complexes can be accompanied by formation of trinuclear clusters [22,27,28]. However, in the case of reactions of the binuclear vinylidene complexes $[\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-C=CHPh})\text{Pt}(\text{L})_2]$ ($\text{L} = \text{PPh}_3, \text{P}(\text{OPr}^i)_3$) with $\text{Co}_2(\text{CO})_8$, the substitution of L by CO occurred without decomposition to give tricarbonyl vinylidene species $[\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-C=CHPh})\text{Pt}(\text{L})(\text{CO})]$ in high yields [23]. These results and potential of such complexes for further synthetic purposes encouraged us to develop methods for introduction of CO ligand in the RePt vinylidene complexes. Therefore, we report here the synthetic approaches to new mixed ligand tricarbonyl complex $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$, as well as its reactivity, molecular geometry, spectroscopic, and electrochemical properties. In this study we also try to evaluate an influence of CO substituent on the properties of the synthesized compound.

2. Experimental

2.1. General considerations

All operations and manipulations were carried out under an argon atmosphere. Reagent grade solvents were dried by the standard procedures, stored under argon, and freshly distilled prior to use. The course of reactions was monitored by TLC on Silufol plates and IR spectroscopy. Neutral alumina and silica gel were used for column chromatography. The X-ray, NMR, and IR data were obtained in the Krasnoyarsk Regional Centre of Research Equipment, Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on the Tensor 27 spectrometer (Bruker, Germany). The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained using NMR spectrometer AVANCE III 600 DPX (Bruker, Germany). The X-ray data were obtained with the SMART APEX II diffractometer (Bruker AXS, Germany). The starting complexes of $[\text{Cp}(\text{CO})_2\text{Re}=\text{C=CHPh}]$ [29], $[\text{Pt}(\text{PPh}_3)_4]$ [30], $[\text{Fe}_2(\text{CO})_9]$ [31] and $[\text{Rh}(\text{acac})(\text{CO})_2]$ [32] were prepared according to the described methods. Preparation of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)_2]$ (2) and $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Fe}(\text{CO})_4]$ was described in [33] and [34]. All other reagents were obtained from commercial sources and used as received. Description of the reactions of complex 1 with PPh_3 , dppe and $\text{Fe}_2(\text{CO})_9$ are included in supplementary material.

2.1.1. Reaction of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-1}\kappa^{\text{C}}\text{:2}\kappa^{\text{C}}\text{-C=CHPh})\text{Fe}(\text{CO})_4]$ with $\text{Pt}(\text{PPh}_3)_4$

$\text{Pt}(\text{PPh}_3)_4$ (90 mg, 0.072 mmol) was added to a solution of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Fe}(\text{CO})_4]$ (41 mg, 0.071 mmol) in 10 mL of benzene and reaction mixture was stirred for 3 hours. The resulting solution was filtered through a pad of SiO_2 (0.5×2 cm) and dried *in vacuo*. The residue was redissolved in hexane and chromatographed on a SiO_2 column (8×2 cm). The column was successively eluted with hexane, hexane-benzene (9:1), (3:2), (1:1) mixtures and benzene.

The first light-pink eluate contained a mixture of $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, which were identified by IR spectra.

The second yellow band after evaporation of solvent and crystallization of a crude product from benzene-hexane mixture (1:1) gave yellow microcrystals of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (1). Yield: 12 mg, 19%.

Anal. Found: C, 46.57; H, 2.89%. *Calc. for* $\text{C}_{34}\text{H}_{26}\text{O}_3\text{P}_2\text{Re}$ (894.84): C, 46.64; H, 2.93%.

IR (CH_2Cl_2 , cm^{-1}): 2030s, 1941s, 1878m (ν_{CO}); (KBr, cm^{-1}): 2034s, 1931s, 1867s (ν_{CO}).

^1H NMR (CD_2Cl_2 , +25°C) δ , ppm [J , Hz]: 5.37 (s, 5H, C_5H_5); 7.04 (m, 1H, $\text{H}_m = \text{C}^2\text{HC}_6\text{H}_5$); 7.12 (m, 2H, $\text{H}_o = \text{C}^2\text{HC}_6\text{H}_5$); 7.20 (m, 2H, $\text{H}_m = \text{C}^2\text{HC}_6\text{H}_5$); 7.41 (s, 1H, $=\text{C}^2\text{HPh}$); 7.46–7.57 (3H, $\text{H}_p + \text{H}_o$, - $\text{P-C}_6\text{H}_5$); 7.62 (m, 2H, H_m , - $\text{P-C}_6\text{H}_5$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25°C) δ , ppm [J , Hz]: 86.2 (s, C_5H_5); 124.6 (s, C_p , $=\text{C}^2\text{HC}_6\text{H}_5$); 126.4 (s, C_m , $=\text{C}^2\text{HC}_6\text{H}_5$); 128.1 (s, C_o , $=\text{C}^2\text{HC}_6\text{H}_5$); 128.3 (d, $^3J_{\text{PC}} = 10.6$, C_m , - PC_6H_5); 130.6 (s, C_p , - PC_6H_5); 132.0 (d, $^2J_{\text{PC}} = 50.3$, $^2J_{\text{PtC}} = 34.7$, C_o , - PC_6H_5); 134.1 (d, $J_{\text{PC}} = 12.5$, $^2J_{\text{PtC}} = 22$, C_{ipso} , -

PC₆H₅); 142.3 (d, ³J_{PC} = 6.5, C_{ipso}, =C²HC₆H₅); 143.2 (d, ³J_{PtC} = 104, ⁴J_{PC} = 5.5, =C²HPh); 196.2 (s, ¹J_{PtC} = 1280, Pt-CO); 202.9 (s, br., 2CO); 229.7 (d, ¹J_{PtC} = 855, μ-C¹).

³¹P{¹H} NMR (CD₂Cl₂, +25°C) δ, ppm [J, Hz]: 31.21 (d, ¹J_{PtP} = 4069).

¹⁹⁵Pt{¹H} NMR (CD₂Cl₂, +25°C) δ, ppm [J, Hz]: -4764 (d, ¹J_{PtP} = 4080).

The third green-brown fraction after removal of solvent gave 32 mg (43%) of cluster [CpReFePt(μ₃-C=CHPh)(CO)₆PPh₃] that identified by IR spectra [27].

IR (C₆H₁₂, cm⁻¹): 2054m, 2039s, 2012s, 1972m, 1959s, 1950m, 1936m, 1923w, 1897m, 1873w (ν_{CO}); (KBr, cm⁻¹): (ν_{CO}); (KBr, cm⁻¹): 2039s, 1997s, 1961sh, 1952s, 1936s, 1913sh, 1870m (ν_{CO}).

The forth yellow fraction was eluted with benzene and after evaporation of solvent gave 25 mg (31%) of [Cp(CO)₂Re(μ-C=CHPh)Pt(PPh₃)₂] (**2**) identified by IR spectra [33].

IR (CH₂Cl₂, cm⁻¹): 1933s, 1858 m, br (ν_{CO}); (KBr, cm⁻¹): 1922s, 1857m (ν_{CO}).

2.1.2. Reaction of [Cp(CO)₂Re(μ-C=CHPh)Pt(PPh₃)₂] with Co₂(CO)₈

100 mg (0.089 mmol) of **2** was dissolved in 10 mL of benzene in a 50 mL two-neck flask, then 31 mg (0.091 mmol) of Co₂(CO)₈ was added. The solution was allowed to stir at room temperature for 2 hours. The solvent was then removed *in vacuo*, the residue was redissolved in hexane-benzene (5:1) mixture and chromatographed on an alumina column (7 × 2 cm). Two fractions were successively eluted with hexane, hexane-benzene (9:1) and (3:2) mixtures. The first brown fraction after evaporation of solvent gave 44 mg (84 %) of yellow-brown complex Co₂(CO)₇(PPh₃) identified by IR spectra. Evaporation of solvent and crystallization of a crude product obtained from the second bright-yellow fraction gave 69 mg (87 %) of [Cp(CO)₂Re(μ-C=CHPh)Pt(PPh₃)(CO)] (**1**) as a yellow crystalline solid.

2.1.3. Reaction of [Cp(CO)₂Re(μ-C=CHPh)Pt(PPh₃)₂] with Rh(acac)(CO)₂

The mixture of 50 mg (0.044 mmol) of complex **2** and a 13 mg (0.050 mmol) of Rh(acac)(CO)₂ were heated at 70°C in 10 ml of benzene for 2 hours. The resulting solution was evaporated, the residue was dissolved in hexane-benzene (5:1) mixture and chromatographed on an alumina column (5 × 2 cm). Two fractions were successively eluted with hexane and hexane-benzene (3:2) mixture. The first yellow fraction after evaporation of solvent gave 22 mg (90 %) of yellow complex Rh(acac)(CO)(PPh₃) identified by IR spectra. The second bright-yellow fraction after evaporation of solvent gave 32 mg (81 %) of yellow complex **1**.

2.2. X-ray diffraction studies of [Cp(CO)₂Re(μ-C=CHPh)Pt(PPh₃)(CO)] (**1**)

Orange crystals of μ₂[(phenylethene-1,1-diyl-1:2κ²C)]-tricarbonyl-1κ²C,2κ¹C-(triphenylphosphane-2κP)-(1-η⁵-cyclopentadienyl)-platinumrhenium(Pt-Re) suitable for X-ray diffraction analysis were grown from a cyclohexane solution under argon atmosphere at -20°C.

C₃₄H₂₆O₃PPtRe·2(C₆H₁₂), monoclinic, C2/c, a=29.424(2), b=13.3719(9), c=24.937(2) Å, β=119.2270(10)°, V= 8562.5(11) Å³, Z=8. The experimental data were collected using fragment of a crystal, dimensions of 0.44×0.28×0.22 mm, with a SMART Apex II diffractometer (Bruker AXS, CCD area detector, graphite monochromator, MoKα radiation, λ = 0.71073 Å, 2θ ≤ 52.74°); 34529 reflections were obtained at 296 K, 8753 are unique. The experimental completeness is 99.8%. Absorption corrections (μ_{Mo} = 6.163 mm⁻¹) have been applied using multiscan procedure [35], R_{int} = 0.0844. The structure was solved by direct methods and refined by full-matrix least squares on F², using SHELXTL program [36]. Hydrogen atoms have been placed in calculated positions and taken into account in the final stages of refinement in the “riding model” approximation. All hexa- and pentagonal cyclic groups were refined in idealized form. The crystal cell contains solvent molecules, two of which are independent. One of them has the shape of a chair and the other is a slightly twisted boat. Refinement converged at a final R1 = 0.0522 for reflections with I_o>2σ_I and 0.1144 for all 8753 data; wR2 = 0.148, GooF = 0.986, 353 refined parameters.

The supplementary crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1431602 The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk> or e-mail: deposit@ccdc.cam.ac.uk.

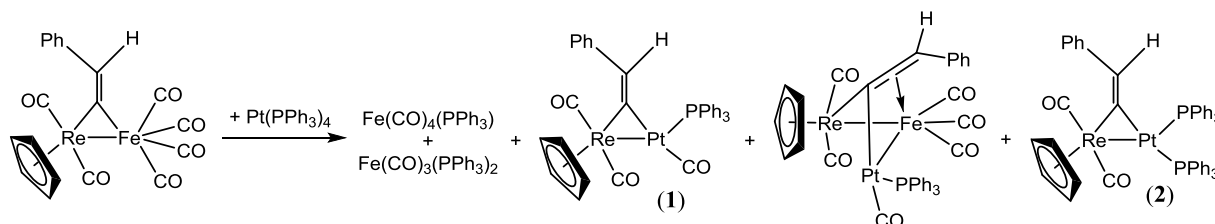
2.3. Electrochemical study

The electrochemical measurements were carried out in acetonitrile solutions with 0.1 M $[\text{Et}_4\text{N}][\text{BF}_4]$ as a supporting electrolyte. The cyclic voltammograms and dc polarograms were recorded on an IPC-Pro M potentiostat (Volta, Saint-Petersburg, Russia) with computer software using a three-electrode system. The working electrode was a stationary platinum electrode of 1 mm diameter or a stationary glassy carbon (GC) electrode of 3 mm diameter in a Teflon housings or a dropping mercury electrode (DME) with a positive margin drop ($m = 3.6 \text{ mg/s}$, $\tau = 0.23 \text{ s}$)². The reference electrode was $\text{Ag}/0.1 \text{ M AgNO}_3$ in MeCN. The auxiliary electrode was a platinum wire. The reference electrode and the auxiliary electrode were separated from the bulk solution in a glass tube filled with an electrolyte solution and fitted with a porous plug. The number of the electrons transferred in a particular redox process was estimated by comparison of the wave height observed with those of the one-electron ferrocene⁺⁰ or $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$ of the same concentration as well as through usual diagnostic electrochemical parameters.

3. Results and discussion

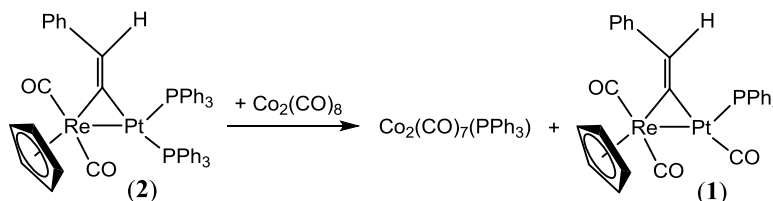
3.1. Synthesis and reactivity of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$

As an extension of our study on synthesis and reactivity of heterometallic vinylidene complexes and clusters, we examined the possibility of synthesizing the known trinuclear cluster $\text{CpReFePt}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_6(\text{PPh}_3)$ [27] in reaction of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Fe}(\text{CO})_4]$ with $\text{Pt}(\text{PPh}_3)_4$. However, this reaction gave not only the expected ReFePt cluster but also an unexpected tricarbonyl heterobimetallic complex $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**1**), which was isolated from the reaction mixture in 19% yield (Scheme 1). The complex $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**1**) is moderately air-stable red-orange crystalline solids, soluble in common organic solvents.



Scheme 1

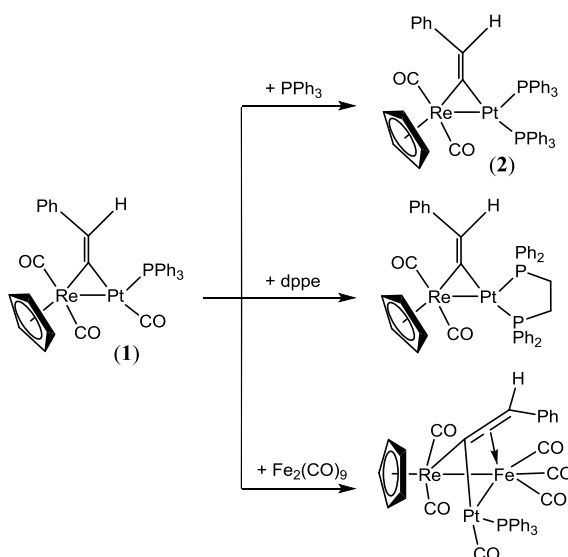
In search of a more efficient and convenient route to the complex **1**, we studied carbonylation reactions of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)_2]$ (**2**). Previously an analogous MnPt complex $[\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**3**) was prepared by the reaction of $[\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)_2]$ and $\text{Co}_2(\text{CO})_9$ [23]. Following these strategy, we attempted to prepare complex **1**. The treatment of **2** with $\text{Co}_2(\text{CO})_9$ (Scheme 2) gave a red-orange solution from which complex **1** was isolated in high yield (87%). The use of $\text{Rh}(\text{acac})(\text{CO})_2$ instead of unstable $\text{Co}_2(\text{CO})_8$ also resulted in obtaining the desired complex, but to reach a quantitative yield of **1** the reaction must be performed in hot benzene for 2 hours.



Scheme 2

² The application of different working electrodes offers an opportunity to study the oxidation and reduction properties of compounds in the extensive potential region. The measurement region of potentials in acetonitrile (vs. $\text{Ag}/0.1 \text{ M AgNO}_3$ in MeCN) is from 0.30 to -3.20 V at DME, from 2.0 to -2.2 V, and from 2.0 to -2.6 V at the Pt and GC electrodes, respectively.

Unfortunately, our attempts to prepare the complex **1** by treating a dichloromethane solution of **2** with a gaseous carbon monoxide were unsuccessful. The traces of **1** in the reaction mixture were only detected by IR monitoring. Such results can be explained by the reverse reaction between **1** and a triphenylphosphane, in which the initial complex **2** regenerates. Indeed, the Pt-bound CO ligand of **1** can be readily substituted upon addition of such nucleophiles like PPh₃ to give the complex **2** in high yield. Displacement of CO and PPh₃ ligands occurs under reaction of **1** with 1,2-bis(diphenylphosphino)ethane to yield the known RePt complex with dppe ligand at the Pt atom [33] (Scheme 3). The formation of both complexes in their reaction mixture was deduced from IR spectra in which a gradual decrease of the high frequency band at 2030 cm⁻¹ and a low-frequency shift of the two ν(CO) bands of the Re-bound carbonyls are observed. The reaction of **1** with Fe₂(CO)₉ results in the formation of the known cluster [CpReFePt(μ₃-C=CHPh)(CO)₆PPh₃] in 92% yield (Scheme 3).



Scheme 3

3.2. NMR and IR study

The IR and the ¹H, ¹³C, ³¹P and ¹⁹⁵Pt NMR data for the complex **1** were obtained. The NMR signals were assigned on the basis of ¹H, ¹³C{¹H} and ¹H, ³¹P{¹H} correlations measured through HSQC and HMQC experiments, respectively. The structure of the complex can be deduced from the combined NMR and IR data, which are similar to those of previously described μ-vinylidene complexes with RePt (**2**) and MnPt (**3**) cores (Table 1) [9,14].

Table 1.

IR and NMR (δ, ppm [J, Hz]) spectroscopic data for the [Cp(CO)₂M(μ-C=CHPh)Pt(PPh₃)L] (M = Re, L = CO (**1**), L = PPh₃ (**2**); M = Mn, L = CO (**3**)). Chemical shifts of second isomer of complex **3** are marked with an asterisk (*).

	IR ^{a)} , ν(CO), cm ⁻¹	NMR ^{b)}							
		¹³ C				¹ H		³¹ P	
		μ-C ¹ =C ² HPh		C ₅ H ₅	CO	=C ² HPh	C ₅ H ₅	P ¹	P ²
		C ¹	C ²						
1	2030 s, 1941 s, 1878 m	229.7 s ¹ J _{PtC} = 855	143.2 d ² J _{PtC} = 104 ³ J _{PC} = 5.5	86.2 s	196.2 s ¹ J _{PtC} = 1280 202.9 s, br ^{c)}	7.41 s	5.37 s	31.21 s, J _{PtP} = 4069	-
2	1933 s, 1858 m,br	232.2 d ¹ J _{PtC} = 821.6 ² J _{PC} = 65.3	138.3 dd ² J _{PtC} = 96.2 ³ J _{PC} = 4.0	85.7 s	204.5 s, br	- ^{c)}	4.81 s	39.29 d, ² J _{PP} = 21.6 J _{PtP} = 4609	28.14 d, ² J _{PP} = 21.6 ² J _{PtP} = 2607
4	2032 s 1938 s, 1871 m	260.5 d ¹ J _{PtC} = 916.9 ² J _{PC} ≤ 2.5	146.3 d ² J _{PtC} = 123.4 ³ J _{PC} = 4.5	85.1 s	195.8 d ¹ J _{PtC} = 1270.9 ¹ J _{PC} = 2.7 228.1 br 232.5 br	7.7 d ⁴ J _{PH} = 11.9 ³ J _{PH} = 40.5	4.72 s	36.5 d, J _{PtP} = 3966	-

- a) In CH₂Cl₂ solution;
- b) In CD₂Cl₂ solution (**1**, **2**) CDCl₃ (**4**)
- c) The =C²HPh signal is masked by the resonances of phenyl groups

The IR spectra of **1** in CH₂Cl₂ solution shows two $\nu(\text{CO})$ bands (1941, 1878 cm⁻¹) that are attributed to the carbonyl groups at the Re atom. The Pt-bound CO in the spectrum of **1** gives rise to an addition absorption at 2030 cm⁻¹.

In the ¹H NMR spectrum a singlet due to the vinylidene proton =C²H is found at δ 7.41. In the ¹³C NMR spectrum of **1** a signal for the bridged C¹ atom of the vinylidene is observed at δ 229.7 with a J_{PtC} coupling of 855 Hz, and this signal is upfield shifted by approximately 31 ppm relative to that of the corresponding MnPt complex (**3**). A doublet at δ 143.2 (with ² J_{PtC} and ³ J_{PC} couplings of 104 Hz and 5.5 Hz, respectively) arises from the C² atom of vinylidene ligand. Similar chemical shifts of signals of the phenylvinylidene ligand in the ¹H and ¹³C NMR spectra were earlier reported for the previously described μ -vinylidene complexes [17,18,33].

The ¹³C NMR spectrum of **1** contains a broad resonance at δ 202.9 that was assigned to the two Re-bound CO ligands. Such line broadness of the CO resonances can be explained by a site exchange of two carbonyl groups of the [Cp(CO)₂Re] fragment and observed earlier [33,37–40]. The presence of one CO coordinated to the platinum atom in the ¹³C NMR spectrum is indicated by a signal at δ 196.2 with a J_{PtC} coupling of 1280 Hz. Comparison of the ¹³C NMR spectra parameters of **1** with those of the previously synthesized heterobinuclear vinylidene, carbyne and carbene complexes containing the Pt-bound CO groups revealed a dependence of the chemical shift of the platinum bound carbonyl group on its position toward a bridging hydrocarbon ligand. For example, in the ¹³C NMR spectra of [(CO)Pt(μ -dppm)(μ -C(OMe)C₆H₄Me-4)W(CO)₄] [41], [(CO)₄W(μ -dppm)(μ -C=CH₂)Pt(CO)] [18] and [(CO)₃Fe(μ -C=CHR)(μ -dppm)Pt(CO)] (R = Ph, *t*-Bu) [17] complexes in that the Pt-bound CO groups are in *cis* to the bridging ligand and *trans* to the second metal-containing fragment, the corresponding signals of the CO groups are observed in the ranges of δ 185–189 ppm. On the other hand, in the analogues manganese complex **3** and the μ -carbyne complexes [Cp(CO)₂W(μ -CR)Pt(CO)(L)] (R = C₆H₄Me-4, L = PMe₃, PMe₂Ph, PPh₃; R = C₆H₃Me-2,6, L = P(Prⁱ)₃) [19,20], with the Pt-bound carbonyl located *trans* to vinylidene, the chemical shifts of the corresponding carbonyls are observed in the region of δ 195 – 199 ppm.

The position of PPh₃ and CO ligands in **1** can also be unambiguously deduced from the ³¹P NMR data. In the previous works [25,33], signals in the ³¹P NMR spectra with a larger coupling constant are assigned to the phosphorus ligand *trans* to metal-containing fragment and the signals with a smaller J_{PtP} coupling are assigned to the ligand *trans* to the μ -C=CHPh. In the ³¹P NMR spectrum of **1** the coupling constant J_{PtP} of a signal of the PPh₃ ligand is comparable to those that were found for phosphorus-containing ligands that are *trans* to [Cp(CO)₂M] fragments of the structurally well-defined vinylidene MnPt and RePt complexes [23,33,42]. So the *trans* position of PPh₃ ligand to [Cp(CO)₂Re] fragment in **1** is indicated by singlet with a J_{PtP} coupling of 4069 Hz at δ 31.2 in the ³¹P NMR spectrum (Table 1).

3.3. Crystal structure

The molecular structure of [Cp(CO)₂Re(μ -C=CHPh)Pt(PPh₃)(CO)] (**1**) was solved on the base of X-ray diffractometry. Suitable crystals of **1** were grown from cyclohexane/hexane mixture. The view of the structure is shown in Fig.1. Selected bond distances and angles of **1** and the corresponding data for **2** are included in supplementary material for comparison purposes (Table S1). Crystal data and refinement parameters are shown in Table 2.

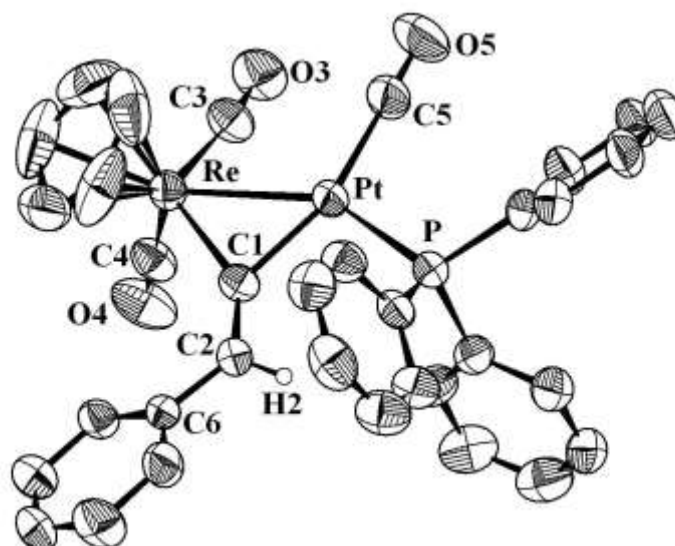


Fig. 1. Molecular structure of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**1**). All hydrogen atoms except that of the phenylvinylidene ligand are omitted for clarity.

Table 2.

Crystal data and X-ray experimental details for complex **1**

Empirical formula	$\text{C}_{34}\text{H}_{26}\text{O}_3\text{PPtRe}\cdot 2(\text{C}_6\text{H}_{12})$
Formula weight	1063.12
Temperature/K	296
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{\AA}$	29.424(2)
$b/\text{\AA}$	13.3719(9)
$c/\text{\AA}$	24.937(2)
$\alpha/^\circ$	90.00
$\beta/^\circ$	119.227(10)
$\gamma/^\circ$	90.00
Volume/ \AA^3	8562.5(11)
Z	8
$d_{\text{calc}}/(\text{g}\cdot\text{cm}^{-3})$	1.649
μ/mm^{-1}	6.163
$F(000)$	4144
Crystal size/ mm^3	$0.44\times 0.28\times 0.22$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	52.74
Reflections collected	34529
Data/restraints/parameters	8753/18/353
Goodness-of-fit on F^2	0.986
Final R_1 [$I \geq 2\sigma(I)$]	0.0522
Final R_1, wR_2 [all data]	0.1206, 0.1480
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ ($\text{e}/\text{\AA}^3$)	-0.90/1.01

The Re- and Pt-containing moieties of the complex are bridged by the μ -vinylidene ligand to give a cycle RePtC1 with the Re-C1 and Pt-C1 distances of 2.065(10) and 2.024(10) Å, respectively. The C1=C2 bond length is 1.330 Å. The $\mu\text{-C=CHPh}$ ligand is located in a plane of carbodimetallacycle; a dihedral angle between the ReC1Pt and C1C2C6 planes is 5.3(11)°. The short Re-Pt distance of 2.7187(6) Å indicates a metal-metal bond in the complex [43]. The bond angles Re-C1-Pt, C1-Pt-Re and Pt-Re-C1 are 83.3(4), 49.0(3) and 47.7(3)°, respectively.

The rhenium atom is coordinated by a η^5 -cyclopentadienyl ligand and by two CO groups. The first carbonyl is terminal and forms an almost linear Re-C4-O4 angle of 177.6(10)°. The Re-C4 and C4-O4 bonds distances are 1.885(12) and 1.162(12) Å, respectively. The Re-C3-O3 angle of the second carbonyl is 171.8(11)°. The length of Re-C3 and C3-O3 bonds are 1.908(12) and 1.171(13) Å, and they are longer than those of the first carbonyl by 0.023 and 0.009 Å, respectively. These geometric parameters of the C3O3 group might be interpreted as indicating a weak Pt→C3O3 semibridging interaction. However, the Pt-C3 distance of 2.747(13) Å is too long to represent any bonding interactions between the adjacent platinum atom and C3O3 group. This bond distance is longer than those found for the RePt complexes with a weak semibridging interaction [33]. Therefore, the C3O3 ligand is just leaning toward the Pt atom and the rhenium-bound carbonyls should be considered as terminal.

The geometry around the platinum atom is a distorted square planar. The PPh_3 and CO ligands form with RePt axis P1-Pt-Re and C5-Pt-Re angles of 146.63(7) and 113.0(4)°, respectively. The Pt-P1 distance of 2.274(3) Å is typical, the same distances were found in previously described μ -vinylidene complexes [33]. The platinum-bound CO ligand forms a linear Pt-C5-O5 angle of 178.2(15)°. The Pt-C5 and C5-O5 bond distances are 1.926(13) and 1.102(12) Å, respectively. They are unusual and considerably differ from corresponding bond distances that were found in another heterobinuclear hydrocarbon bridged complexes containing the platinum-bounds carbonyl ligands, for example, $[(\text{P}^i\text{Bu}_3)(\text{CO})\text{Pt}(\mu\text{-H}_2\text{CCPh})\text{Os}(\text{SnPh}_3)(\text{CO})_4]$ (1.882(4) and 1.134(6) Å) [44], $[(\text{PPh}_3)(\text{CO})\text{Pt}(\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-C(Ph)=C=CH}_2)\text{Ru}(\text{CO})\text{Cp}]$ (1.882(10) and 1.140(12) Å) [22]. However, there are complexes in which the similar Pt-C and C-O bond lengths are found, for example, a homobinuclear vinylidene complex $[\text{cis,cis-Pt}(\text{C}_6\text{F}_5)_2(\text{CO})(\mu\text{-C=CHPh})\text{Pt}(\text{PPh}_3)_2]$ (1.924(8) and 1.116(8) Å) [15] and a trinuclear carbyne cluster $[\text{Pt}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PMePh}_2)_2(\eta\text{-C}_5\text{H}_5)]$ (1.83(5) and 1.11(7) Å) [19]. Such elongation of Pt-C5 and shortening of C5-O5 bond length are probably a consequence of a strong electron-withdrawing ability of the phenylvinylidene ligand that is *trans* to C5O5 group. The electron-withdrawing character of vinylidene and related hydrocarbon ligands has been also observed in other heterobimetallic complexes containing $[\text{PtL}_2]$ ($\text{L} = \text{PPh}_3$ (**2**), PMe_3 , PMe_2Ph , PMePh_2 ; $\text{L}_2 = \text{dppm}$, dppe , dppp) fragments [17,22,25,33,45]. For example, the two Pt-P distances in **2** are unequal (Pt-P1 = 2.272(1) and Pt-P2 = 2.375(1) Å), a longer Pt-P2 bond distance for the phosphorus atom is *trans* to the bridged vinylidene, and a short Pt-P1 bond distance is *trans* to the $[\text{Cp}(\text{CO})_2\text{Re}]$ fragment [33]. Significantly, it is a PPh_3 *trans* to vinylidene that undergoes substitution by CO in the complex **2**; the other PPh_3 ligand *trans* to $[\text{Cp}(\text{CO})_2\text{Re}]$ fragment remains bound to the Pt atom after carbonylation.

The presence of CO at the Pt was found to slightly influence the geometrical parameters of the carbodimetallacycle and the vinylidene ligand of **1** in comparison with the RePt complexes with chilate diphosphine and two PPh_3 (**2**) ligands. Comparison of the structure features of **2** and **1** revealed that on passing from **2** to **1** the Re-C1 and C1=C2 bond distances decrease from 2.083(5) and 1.351(6) Å to 2.065(10) and 1.330(12) Å, respectively, whereas the Pt-C1 bond length increases from 2.008(4) to 2.024(10) Å. The RePt bond distance in **2** is by 0.017 Å shorter than that in **1**. The changes in the bond angles Re-C1-Pt, C1-Pt-Re and Pt-Re-C1 of the carbodimetallacycle are minor. Despite some differences in geometrical parameters between **2** and **1**, an overall geometry of complex **1** is therefore close to that of the μ -vinylidene RePt complexes described previously [33].

3.4. Electrochemistry

The redox properties of complex **1** were studied by cyclic voltammetry (CV) at platinum or glassy carbon (GC) electrodes and by dc polarography at a dropping mercury electrode (DME) in

acetonitrile solutions. Potentials are given versus Ag/0.1 M AgNO₃ in MeCN (they can be converted to V versus SCE by adding 0.337 V).

The complex [Cp(CO)₂Re(μ-C≡CHPh)Pt(PPh₃)(CO)] (**1**) exhibits at the GC-electrode two one-electron oxidation stages ($E_{1/2} = 0.18, 1.02$ V) and one-electron reduction stage ($E_{1/2} = -2.32$ V) (Fig. 2 – solid line). At the Pt-electrode the CV shows only two one-electron oxidation stages at $E_{1/2} = 0.17$ and 1.07 V. First oxidation waves at the Pt and GC-electrodes (Fig.2 – dotted line, peaks A₁ and A₁') are electrochemically quasi-reversible³. The reduction of **1** at the GC-electrode is electrochemically quasi-reversible⁴ (Fig.2, peaks A₃, A₃'). At the DM electrode **1** shows three reduction waves at $E_{1/2} = -2.33, -3.00$ and -3.10 V, respectively.

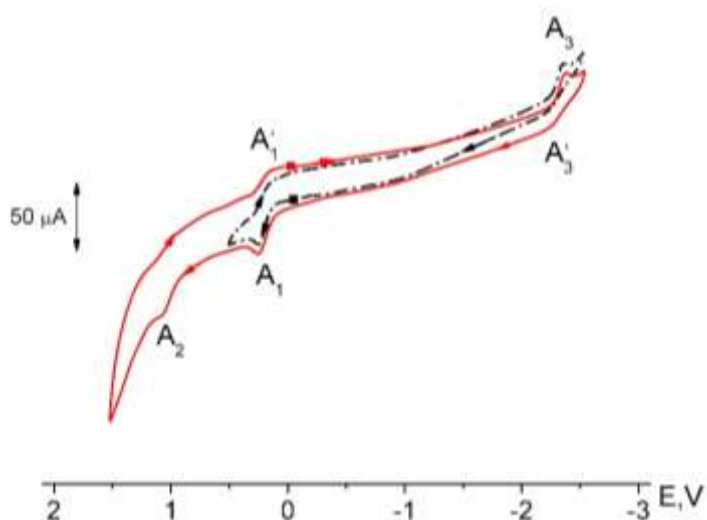


Fig. 2. The cyclic voltammograms of **1** at GC-electrode in MeCN (0.1 M Et₄NBF₄, C = 2 mM, scan rate 25 mV s⁻¹, potentials vs. Ag/0.1 M AgNO₃ in MeCN) (solid line – the initial negative potential sweep, dotted line – the initial positive potential sweep).

In our previous work [46], more negative oxidation ($E_{1/2} = -0.07, 0.26, 0.33$ V at the Pt electrode) and reduction ($E_{1/2} = -2.60, -2.80$ и -3.00 V at the DME) potentials are found for the complex [Cp(CO)₂Re(μ-C≡CHPh)Pt(PPh₃)₂] (**2**), which are apparently caused by a strong donating character of PPh₃ ligand. Comparison of the electrochemical behavior of **1** and **2** showed that replacement of more electron rich PPh₃ ligand in **2** by CO resulted in anodic shift of $E_{1/2}$ values of **1**. Moreover, the first oxidation of **1** are quasi-reversible at the Pt- and GC-electrodes. Under the same CV conditions **2** undergoes an irreversible oxidation at 0.33 V, this half wave oxidation potential value coincides with the oxidation potential value ($E_{1/2} = 0.33$ V) of a mononuclear complex Cp(CO)₂Re=C≡CHPh [46]. This demonstrates that the one electron oxidation of **2** results in the mononuclear complex, which is clearly confirmed by the presence of two ν(CO) bands 1994 and 1920 cm⁻¹, corresponding to Cp(CO)₂Re=C≡CHPh in the IR spectra of the solutions obtained after the controlled potential electrolysis of **2**, or by the isolation of Cp(CO)₂Re=C≡CHPh in quantitative yields after the reaction of **2** with [Cp₂Fe][BF₄]. In contrast to [Cp(CO)₂Re(μ-C≡CHPh)Pt(PPh₃)₂], no oxidation peaks of the mononuclear decomposition product was detected for complex **1** (Fig.2 – solid line), indicating the greater electrochemical stability of the last one relative to **2**.

³ The ratio of cathodic to anodic peak currents $I_{pc}/I_{pa} = 0.75$ ($I_{pc} = 14.01$, $I_{pa} = 18.62$), $\Delta E = |E_{pa} - E_{pc}| = 136$ mV (Fig.2, peaks A₁, A₁')

⁴ The ratio of the anodic to cathodic peak currents $I_{pa}/I_{pc} = 0.51$ ($I_{pa} = 14.30$, $I_{pc} = 27.80$), $\Delta E = |E_{pc} - E_{pa}| = 89$ mV (Fig.2, peaks A₃, A₃') at GC-electrode and $I_{pa}/I_{pc} = 0.76$ ($I_{pa} = 2.97$, $I_{pc} = 3.91$), $\Delta E = |E_{pc} - E_{pa}| = 165$ mV at Pt-electrode

4. Conclusion

Three synthetic methods were attempted to prepare the complex **1**. The most convenient and high-yield approach to $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)(\text{CO})]$ (**1**) is based on the reactions of $[\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Pt}(\text{PPh}_3)_2]$ (**2**) with $\text{Co}_2(\text{CO})_8$ or $\text{Rh}(\text{acac})(\text{CO})_2$. Remarkably, these reactions led to the selective substitution of the Pt-bound triphenylphosphine being in *trans*-position to vinylidene ligand with CO. Such reactivity of the initial complex **2** reflects the *trans*-influence of the vinylidene ligand.

The spectroscopic, structural and electrochemical features of **1** were described. Comparison of spectroscopic, XRD and electrochemical data of **1** with those of the previously synthesized binuclear vinylidene bridged complexes was carried out. The presence of the Pt-bound CO ligand slightly influences on the spectroscopic properties of the complex. The overall geometry of complex **1** is similar to those of the previously described μ -vinylidene heterometallic complexes. At the same time, the geometric parameters and ^{13}C NMR data for the platinum-bound CO ligand of **1** differ from those of the another complexes containing the platinum-bound CO ligand. Such features of **1** arise from the *trans*-position of the CO group to the strong electron-withdrawing phenylvinylidene ligand. Significant changes are observed in electrochemical properties of **1**, the electron-withdrawing carbonyl and vinylidene ligands makes the RePt core of **1** electron deficient and, consequently, resistant to oxidation in comparison to the previously described RePt μ -vinylidene complexes.

Acknowledgements

The reported study was funded by the State budget allocated to the fundamental research in the Russian Academy of Sciences in the framework of Project No. V.44.1.7 and was financially supported by Krasnoyarsk Region Science and Technology Support Fund (the junior scientists project no. 3/15).

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